585. *Factors influencing the Rates of Dissociation of Metal Complexes. Part III.*[1] *The Dissociation of Bis(ethylenediamine)- and Tris(ethylenediamine)-nickel Complexes and of the Racemic 2,3-Diaminobutane Analogues.*

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The kinetics of dissociation of $[NiA_2(H_2O)_2]^{2+}$ and $[NiA_3]^{2+}$ (A = ethylenediamine or racemic 2,3-diaminobutane) in aqueous acid have been investigated by the stopped-flow method. The results, with those for $[NiA(H_2O)_4]^{2+}$ obtained previously, show that differences in dissociation rates for the tris-, bis-, and mono-species (which reside in the energy of activation values) account largely for differences in formation constants for the three species. It appears, from the limited data available, with other nickel complex systems also, that the formation rate constants for successive species are very similar. A blue and a yellow form of bis-(racemic 2,3-diaminobutane)-nickel(II) ion in solution are discussed.

We have previously measured the rates of dissociation of mono(ethylenediamine)nickel ion and related complexes.[1] The rates with the higher nickel complexes of aliphatic diamines are known to be much faster [2,3] and their measurement in aqueous solution requires special methods.[4] We now describe the determination of the rates of dissociation, in excess of acid, of tris(ethylenediamine)- and bis(ethylenediamine)-nickel ions:

$$[Ni(en)_3]^{2+} + 2H_3O^+ \longrightarrow [Ni(en)_2(H_2O)_2]^{2+} + (en)H_2^{\,2+}$$
$$[Ni(en)_2(H_2O)_2]^{2+} + 2H_3O^+ \longrightarrow [Ni(en)(H_2O)_4]^{2+} + (en)H_2^{\,2+}$$

We have examined also the complexes of racemic 2,3-diaminobutane ("butylenediamine," abbreviated bn), since their rates are slower, and can be measured more accurately. The stopped-flow apparatus [5] was used, in which acid and complex ion were rapidly mixed, the flow of the mixed solution suddenly arrested, and the optical density of the reacting solution recorded on an oscilloscope. The molar absorption coefficients of the complex ions are relatively small in the visible region (see Fig. 1) and their concentration must exceed about 0·01M to provide reasonable optical density changes during reaction. For this reason, the rate of dissociation in acid concentrations less than 10^{-2}M cannot be followed spectrally, and only bis(butylenediamine)nickel(II), of the ions investigated, dissociates slowly enough at 0° for the rate to be followed at higher pH values by measuring the consumption of acid added to maintain a constant pH.[1] We were not able therefore to study the detailed mechanism of dissociation of these ions (unlike the mono-series) although some semiquantitative observations were possible.

Experimental

Stopped-flow Method.—Gibson's apparatus [5] was used. Amines were redistilled before use and all solutions were thoroughly degassed, otherwise gas bubbles which developed interfered with the spectral observations. Equal amounts of the complex solution (0·05M-nickel ion, 0·15—0·18M-amine) and acid (0·4—2·0M) were contained in two separate 2 c.c. syringes and delivered rapidly to a mixing chamber and thence to an observation tube (20 mm. light path) which was fitted with a device for arresting the flow of liquid within about one millisecond. Both mixing and observation chambers could be controlled by thermostat to ±0·1°. At the point of stopped-flow, the reaction proceeded to completion. As the optical density of the

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[1] Ahmed and Wilkins, Part I, *J.*, 1959, 3700; Part II, preceding paper.

[2] Wilkins, *J.*, 1957, 4521.

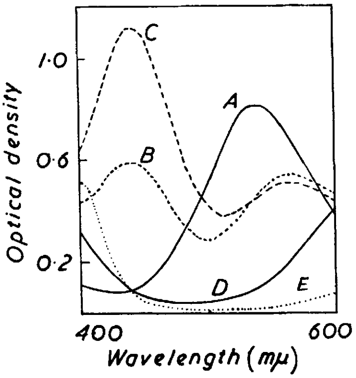
[3] Bjerrum, Poulsen, and Poulsen, "Proceedings of the Symposium on Co-ordination Chemistry," Danish Chemical Society, 1954, p. 51.

[4] See, *e.g.*, Roughton and Chance in "Investigation of Rates and Mechanisms of Reactions," ed. Friess and Weissberger, Interscience Publ. Inc., New York, Chapter 10.

[5] Gibson, *Discuss. Faraday Soc.*, 1954, **17**, 137.

solution changed, the intensity of light (provided by a monochromator, 390—650 mμ range) transmitted through the observation chamber changed. This caused proportional changes in current in a linked photomultiplier and these were fed into an oscilloscope, and the trace was photographed. The completion of the reaction was shown on a pen recorder, used in conjunction with the oscilloscope. Half-lives exceeding about 1 sec. could be estimated with reasonable accuracy from the pen-recorded trace. Typical oscilloscope traces are reproduced in Fig. 2 (curves *A* and *B*) which also show the base line drawn in at the completion of the

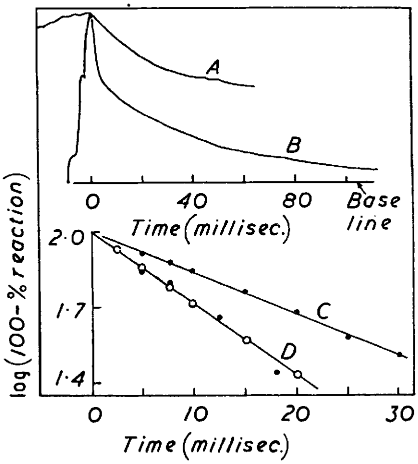
FIG. 1. *Spectra of nickel*(II)-(*racemic* 2,3-*diaminobutane*) *complexes between* 400 *and* 600 *m*μ.



A, 0·025M-Ni²⁺, 0·090M-amine. *B*, 0·025M-Ni²⁺, 0·050M-amine (nitrate). *C*, 0·025M-Ni²⁺, 0·050M-amine (1M-perchlorate). *D*, 0·075-Ni²⁺, 0·025M-amine (0·05M-Ni²⁺ " blank "). *E*, 0·025M-Ni²⁺.

(*All spectra in* 40 *mm. cells.*)

FIG. 2. *Typical oscilloscope traces and accompanying first-order curves.*



A and D (*open circles*), *Run* 5. *B, C, and D* (*full circles*), *Run* 8. (*The time-abscissa should be multiplied by ten for B and C.*)

TABLE 1. *Dissociation of* $[\mathrm{NiA}_n]^{2+}$ *ions in acid.*

Run no.	Dissociating species	Temp.	Acid (M) *	*k* (sec.⁻¹)
1	$[\mathrm{Ni(en)_3}]^{2+}$	7·5°	0·2	14·1
3		7·8	0·2	12·6
4		21·8	0·2	61·4
5		21·8	0·2	64·2
6		21·8	0·2	63·0
7 [a]		21·8	0·2	60·8
8 [a]		21·8	0·2	66·7
15		27·1	0·2	82·5
11		21·8	1·0	54·2
12		21·8	1·0	55·5
2 [b]	$[\mathrm{Ni(en)_2}]^{2+}$	7·6	0·15	0·66
3		7·8	0·15	0·67
7 [a]		21·8	0·15	3·94
8 [a]		21·8	0·15	3·69
9 [c]		21·8	0·15	3·61
10 [c]		21·8	0·15	3·98
11		21·8	1·0	4·28
12		21·8	1·0	4·44
13 [d]		21·8	0·15	3·43
14 [d]		21·8	0·15	3·33
16 [c]		27·1	0·15	6·24
14 [d]	$[\mathrm{Ni(en)}]^{2+}$	22·4°	0·10	0·109
14A [d]		21·8	1·00	0·173
17	$[\mathrm{Ni(bn)_3}]^{2+}$	7·8	0·225	1·76
18		7·8	0·225	1·85
19		18·4	0·225	4·71
20		18·4	0·225	4·71
21	$[\mathrm{Ni(bn)_2}]^{2+}$	0·9	0·175	0·0257
18 [b]		7·8	0·175	0·0477
19 [b]		18·4	0·175	0·147
20 [b]		18·4	0·175	0·132
22 [e]		0·6	0·074	0·020
23 [f]		0·6	0·071	0·022
24 [f]		0·6	0·074	0·021
25 [f]		0·6	0·74	0·025
26 [f]		0·6	1·56	0·031
27		0·6	10^{-4}	0·024

* Acidity at commencement.

[a] Slower oscilloscope time base to record better bis ——▶ mono change (less accurate for tris ——▶ bis). [b] Using pen recorder. [c] Commencing solution containing mainly $[\mathrm{Ni(en)_2}]^{2+}$.

All observations at 520 mμ except: [d] Observation wavelength 570 mμ. [e] Observation wavelength 560 mμ. [f] Observation wavelength 445 mμ.

reaction. The height of the curve above this line is a measure of $(I_0 - I_t)$, allowance being made for a small residual optical density of nickel ion produced by the reaction. A quantity $\propto I_0$ can be superimposed on the oscilloscope trace. The ascending curve on the extreme left represents the increase of optical density as spent solution is replaced by reacting solution in the period between flow starting and stopping. Curve *B* was obtained with a slow oscilloscope time basis (1·5 sec.) and shows clearly the two dissociative steps involving tris- and bis-species and the tailing off due to the final change from mono-species. Since the associated rate constants differ appreciably, analysis of the first two portions of the curve is straightforward, and yields linear semilogarithmic plots (*C* and *D*; full circles). The extent of reaction is obtained from the optical density ($=\log I_0/I_t$). When a faster time basis was used (0·15 sec.), curve *A* was obtained, showing only the dissociation of the tris-complex, from which an accurate rate constant was obtained (curve *D*, open circles). The optical density of each species, estimated from these rate curves, agreed well with the known value. In the experiments in 0·2M-perchloric or 0·225M-nitric acid an appreciable amount of acid was consumed by the liberated amine, but the rate varies only very slightly with pH in this region, as shown also by the linearity of the first-order plots.

The results are shown in Table 1. Runs 1—20 were obtained with the stopped-flow apparatus, and the remainder (except 27) by normal spectrophotometry.[1] An ionic strength of 1·0M, with added sodium perchlorate, was used in runs 1—16 and 23—25, and an ionic strength of 0·5M, with added sodium nitrate, in runs 17—21 and 27. In runs 22 and 26 no salts were added, only perchlorate anion being present.

Additional experiments on $[Ni(en)]^{2+}$ using a pen recorder (runs 14 and 14A) were included to increase the temperature range previously studied.[1] In run 27 using a pH-stat, the equilibrium consumption of acid was calculated on the basis of the loss of *one* of the two amines of $Ni(bn)_2]^{2+}$. The dissociation of $[Ni(bn)]^{2+}$ is negligible in the early stages of the bis-dissociation and this early portion was used in the estimation of the first-order rate constant. For the determination of Arrhenius parameters the following were used: runs 1 and 3—6, $[Ni(en)_3]$; runs 2, 3, 7—10, 16, $[Ni(en)_2]$; runs 17—21 for the butylenediamine complexes.

DISCUSSION

Two Forms of Bis(diamine)nickel Complexes.—It has been known for some time that yellow and blue forms of bis(diamine)nickel complexes, often interconvertible, can exist both in the solid state and in solution.[6] The blue form is considered to be an octahedral complex, containing the two bidentate groups and two other groups which may be *cis* or *trans* to one another and which in the common case will be two water molecules. The yellow form has essentially a four-covalent planar structure. It was necessary to examine our complexes for such forms as a precursor to our kinetic studies. The spectrum of a mixture of nickel ions and butylenediamine (1 : 2, and therefore mainly bis) between 400 and 600 mμ is shown in Fig. 1 (curve *B*). The yellow and blue bands at 442 mμ and 564 mμ, respectively, are apparent. The intensity of the former increases with increase in temperature and almost two-fold in 1M-sodium perchlorate (curve *C*), while the other decreases slightly. Above 1·5M-sodium perchlorate, a yellow solid, $[Ni(bn)_2](ClO_4)_2$ is precipitated. The spectral behaviour resembles closely that reported by Jörgensen[7] for $[Ni(trien)](NO_3)_2$ (trien = triethylenetetramine) and, after this work was completed, by Sone and Kato[8] for bis(ethylenediamine)- and bis(propylenediamine)-nickel ions. The yellow band is, however, more marked with the butylenediamine complex, perhaps not surprisingly since with complete *C*-methylation of en, in $[Ni(tetraMeen)_2]^{2+}$, only a yellow form exists in solid or solution.[9] It can be estimated from the change in optical density at 564 mμ with curves *B* and *C* that about 5% of bis-species is present in the solution without added perchlorate. A similar rate of dissociation of $[Ni(bn)_2]^{2+}$ is obtained from observations at 445 mμ and 560 mμ (runs 22—24) and extrapolation of each first-order

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[6] For literature and discussion on ligand-field basis see Ballhausen and Liehr, *J. Amer. Chem. Soc.*, 1959, **81**, 538.

[7] Jörgensen, *Acta Chem. Scand.*, 1957, **11**, 399.

[8] Sone and Kato, *Z. anorg. Chem.*, 1959, **301**, 277.

[9] Basolo, Chen, and Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 956.

plot to zero time gives the expected optical density. This proves that both bands arise from a bis-species. A simple experiment shows that the *cis-trans*-isomerisation involving the bis-species must be labile and intramolecular. If acid is added to violet $[Ni(bn)_3](NO_3)_2$ in solution at 0° and within 5—10 sec., when the tris- has been converted to the " blue " bis-complex, 1M-sodium perchlorate at 0° is added, a yellow solution is formed without noticeable delay. Removal of one ligand from the tris- must leave the bis-complex in a *cis*-form, and since the yellow form is *trans*, the rearrangement must be rapid. It cannot operate *via* dissociation of the bis-species because this is much slower. The relevant portion of the spectra of the other butylenediamine complexes, which resemble closely those of ethylenediamine, are shown in Fig. 1. Possible complications due to the two forms of bis-complexes and consideration of spectral changes demanded a wavelength of 520 mμ for following the tris ⟶ bis ⟶ mono change for both complexes. The dissociation of $[Ni(en)_2]^{2+}$ was also studied at 570 mμ, the approximate isosbestic point for the tris- and bis-species. The results agreed with that at 520 mμ, and confirmed our assignment of species changes to the dissociation traces, but were not sufficiently accurate for use in determining Arrhenius parameters. At 570 mμ, $[Ni(en)]^{2+}$ absorbs sufficiently for its dissociation to nickel ions (subsequent to bis-dissociation) to be studied, and the rate agrees well with that expected from our measurements with a simpler apparatus.[1]

Dissociation Data.—The results, together with those for the mono-species,[1] are collected in Table 2. Perchloric acid was used to dissociate the ethylenediamine complexes to avoid possible anionic acceleration effects, but because of solubility difficulties it was necessary to use nitric acid for the higher butylenediamine species. Previously[1] it had been shown that there is an increase in the rate of dissociation of $[Ni(\textit{rac}\text{-bn})]^{2+}$ in nitric acid compared with perchloric acid, and, for the latter the Arrhenius parameters are 19·4 kcal./mole and log A = 12·4 (sec.$^{-1}$). Thus the results for the ethylenediamine and butylenediamine complexes can be compared despite the difference in anion medium. The agreement with measurements in methanol[3] is as good as can be expected.[10] As far as was possible it was shown that bis(butylenediamine)nickel ion behaved like mono(ethylenediamine)-nickel ion. The rate constant does not vary between pH = 4 and 1 (runs 23, 24, and 27). In the mono-series (and presumably here also) this value refers to the rate of first bond rupture. The rate then increases in higher acid concentration (runs 9—12, 23—26). The detailed mechanism for the dissociation of the tris- probably also resembles that of the mono-complex: the rate of dissociation of $[Ni(en)]^{2+}$ in dilute acid is about 20 times faster than in neutral solution; the factor for $[Ni(en)_3]^{2+}$ ion is about 30, as indicated by considering some earlier exchange data.[11] There is some evidence that after the " limiting " rate of dissociation, further acid has no (or even a slight decelerating) effect with $[Ni(en)_3]^{2+}$ (runs 7, 8, 11, and 12).

TABLE 2. *Kinetic data,* $k_d = A \exp(-E/\mathbf{R}T)$, *for first-order dissociation of nickel–diamine complexes in* 0·2M-*acid at* 25°.

Species	k_d (sec.$^{-1}$)	E (kcal. mole^{-1})	log A (sec.$^{-1}$)	Species	k_d (sec.$^{-1}$)	E (kcal. mole^{-1})	log A (sec.$^{-1}$)
$[Ni(en)_3]$	86·6	18·0 ± 1·2	15·2 ± 0·8	$[Ni(bn)_3]$	8·25	14·6 ± 0·3	11·6 ± 0·4
$[Ni(en)_2]$	5·2	19·8 ± 1·0	15·3 ± 0·6	$[Ni(bn)_2]$	0·257	16·1 ± 0·3	11·2 ± 0·3
$[Ni(en)]$	0·145	20·5 ± 0·6	14·3 ± 0·5	$[Ni(bn)]$	0·020	18·4 ± 0·2	11·8 ± 0·2

The slower rate of the butylenediamine complex compared with its ethylenediamine analogue arises from a much lower A (and $\Delta S^{\ddagger}$) value, partly offset by a lower energy of activation, an effect observed with other *C*- and *N*-alkylethylenediamine complexes.[1] The lower entropy of activation for the substituted amine complex can be ascribed to a relatively higher solvation of the transition state than of the reactant, an explanation which resembles that used to account for large differences in the entropy of reaction of

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[10] Ahmed and Wilkins, *Proc. Chem. Soc.*, 1959, 399.

[11] Popplewell and Wilkins, *J.*, 1955, 4098.

nickel ion with ethylenediamine and with *NN'*-diethylethylenediamine.[1,12] Professor R. G. Pearson has pointed out to us that there is a good analogy between the entropies of activation for the dissociation of the ethylenediamine and the alkyl-substituted ethylenediamine complexes and the entropy changes [13] for the hydrolysis of ammonium ions (~0 e.u.) and trimethylammonium ions (−15 e.u.). The differences in rates of the three species, especially with the more accurate butylenediamine series, is a result solely of activation-energy differences. Combination of the rate constants for dissociation with the formation constants,[9] gives for the formation rate constants at 25° for the ethylenediamine complexes, $10^{-6}k_f = 6$ (mono), 16 (bis), and 9 (tris) l. mole^{-1} sec.$^{-1}$. The changes in the successive stability constants (K) thus arise largely from different dissociation rate constants (k_d), while the formation rate constants remain approximately constant. This behaviour is observed with other nickel systems. Table 3 shows that, for all nickel systems so far examined kinetically, $\Delta \log k_d \approx \Delta \log K$ for pairs of species in a series of complexes. It is perhaps understandable that, in the association process, the rate at which a ligand will replace water in the metal aqua or complex species will not depend seriously on the fact that ligand(s) may be already present, apart from a statistical effect which will tend to slow down successive steps. However, the effect of ligands already present might be expected to be more important on the dissociation rate. For in the simple case of the tris-ethylenediamine complexes, a ligand breaks away from the influence of *trans*-nitrogen atoms but in the mono-form from *trans*-oxygen atoms of water. Although it is not certain yet how the "*trans*-effect" operates kinetically, or indeed whether it is important for complexes of nickel, it is tempting to correlate the decreased rate of the mono- with a weaker *trans*-labilising effect of water compared with ethylenediamine in the tris-complex. Other effects must of course be present, as is seen for example, in the nickel phenanthroline series, although here too the formation rate constant values are very close to one another.[14] Moreover, it is known that in going from $[Fe(phen)_3]^{2+}$ to $[Fe(phen)_2]^{2+}$ we have drastic changes in bond character, as judged by magnetic measurements on $Fe(phen)_3Cl_2,6H_2O$ and $Fe(phen)_2Cl_2$,[15] leading to much greater kinetic stability for the tris-species.[16] This change in the nature of the metal—ligand bond may account for tris(phenanthroline)nickel ions being more stable relative to the mono- [17] than is the case with the diamines and glycine complexes, even although the effect does not show in magnetic changes. It is significant that the same situation applies to the nickel–dipyridyl and cobalt(II)–phenanthroline systems, since the mono-, in each case, is only slightly more stable kinetically than the tris-complex.[18] This should mean that comparable stepwise stability constants will obtain with these systems, and

TABLE 3. *Thermodynamic and kinetic data for the dissociation of nickel complexes at 20—25°.*

Species	log k_d (sec.$^{-1}$)	log K	Species	log k_d (sec.$^{-1}$)	log K
$[Ni(en)_3]^{2+}$	1·95	5·0 [a]	$[Ni(glycine)_2]^0$	1·32 [b]	4·8 [c]
$[Ni(en)_2]^{2+}$	0·72	6·5 [a]	$[Ni(glycine)]^+$	−0·27 [b]	5·8 [c]
$[Ni(en)]^{2+}$	−0·84	7·6 [a]	$[Ni(2\text{-methylpyridylamine})_3]^{2+}$	$\approx$−1·5 [d]	5·1 [e]
$[Ni(bn)_3]^{2+}$	0·92	4·3 [a]	$[Ni(2\text{-methylpyridylamine})]^{2+}$	−3·5 [d]	7·2 [e]
$[Ni(bn)_2]^{2+}$	−0·59	6·5 [a]	$[Ni(phen)_3]^{2+}$	−5·11 [f]	7·6 [g]
$[Ni(bn)]^{2+}$	−1·69	7·7 [a]	$[Ni(phen)_2]^{2+}$	−4·74 [f]	8·1 [g]
$[Ni(glycine)_3]^-$	2·36 [b]	3·6 [c]	$[Ni(phen)]^{2+}$	−5·00 [f]	8·6 [g]

[a] See ref. 9. [b] See ref. 10. [c] Flood and Lorås, *Tidskr. Kjemi Berg.*, 1945, **5**, 83. [d] Unpublished exchange results, and ref. 1. [e] Goldberg and Fernelius, *J. Phys. Chem.*, 1959, **63**, 1246. [f] See refs. 17 and 18. [g] See ref. 14.

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[12] Basolo and Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 211.

[13] Everett and Wynne-Jones, *Proc. Roy. Soc.*, 1941, **177**, *A*, 499.

[14] Margerum, Bystroff, and Banks, *J. Amer. Chem. Soc.*, 1956, **78**, 4211.

[15] Basolo and Dwyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1454.

[16] Lee, Kolthoff, and Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 3596.

[17] Wilkins and Williams, *J.*, 1957, 4514.

[18] Ellis and Wilkins, *J.*, 1959, 299; Ellis, Ph.D. Thesis, Sheffield, 1958.

this is observed experimentally.[19] It matters little whether the rates in acid or neutral solution are compared, since often there is either a small effect of acidity or larger similar effects for each species (see above). It is relevant that Bjerrum and his co-workers[20] estimated that the formation rate constants in the reactions:

$$[Cr(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Cr(H_2O)_5SCN]^{2+} + H_2O$$

and

$$[Cr(H_2O)(SCN)_5]^{2-} + SCN^- \rightleftharpoons [Cr(SCN)_6]^{3-} + H_2O$$

were similar and that different aquation (dissociation) rate constants accounted for the higher stability of the mono(thiocyanato)chromium(III) ion. Only more data for other complexes of nickel, and of other metals, will show how general is this phenomenon.

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[19] Irving, *Chem. Soc. Spec. Publ.*, 1959, No. 13, 13.
[20] Poulsen, Bjerrum, and Poulsen, *Acta Chem. Scand.*, 1954, **8**, 921.